UNIVERSITY OF
CHEMISTRY AND TECHNOLOGY
PRAGUE

Sorption properties of limestones for effective CO_2 removal from flue gas

Marek Staf, Karel Ciahotný, Barbora Miklová

University of chemistry and technology, Prague
Department of gaseous and solid fuels and air protection

Prague, 8th November 2016

Aims of the study and methods

Primary aim: overcoming problems with gradual decrease of sorption capacity

Main field of limestones application = post combustion capture of CO_2 from flue gas

Purpose of the study within the large scale project = collection of technical data about:

- equilibrium sorption capacities,
- technically usable transfer capacities,
- changes in sorption capacities due to number of sorption / desorption cycles,
- efficiency of precautions against capacity decrease,
- investigation of mechanism of structural changes in the limestone grains.

Applied methods:

XRF spectroscopy, measurement of BET surface + pore size distribution, evaluation of sorption properties in fixed bed reactor ... etc.

Sample base

Natural limestones: 11 samples with wide range of properties

Grain zize range used for experiments: 1 – 2 mm

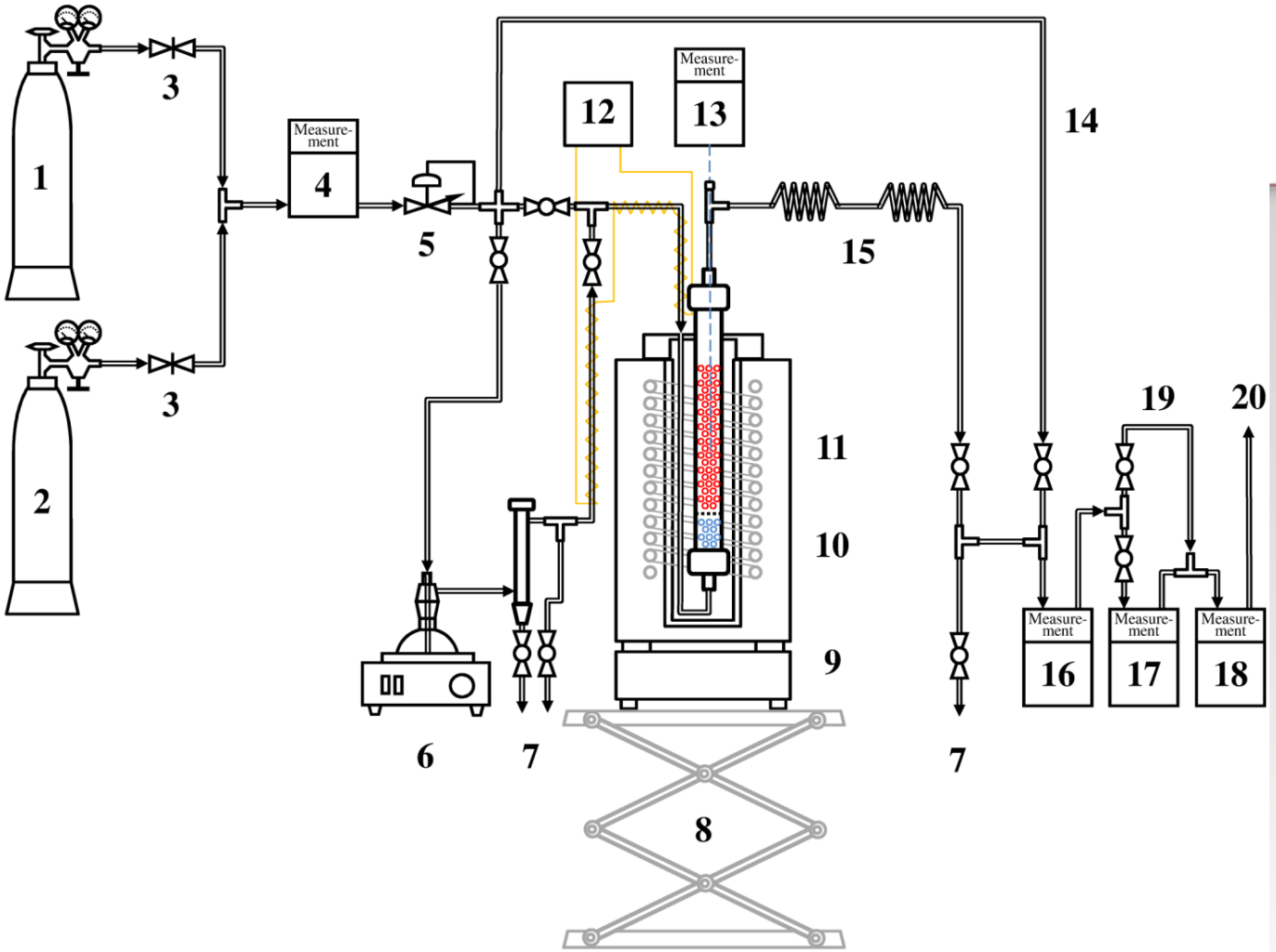
Chemical composition (wt. %):

- Content of $CaCO_3$
  min. 69.3 % max. 98.8 %
- Content of $MgCO_3$
  min. 0.6 % max. 12.5 %
- Content of SiO_2
  min. 0.2 % max. 20.3 %
- Content of Al_2O_3
  min. 0.0 % max. 6.1 %

Apparent density ($g.cm^{-3}$):

min. 2.5 max. 2.9

Experimental apparatus



1 – pressure cyl.
2 – pressure cyl.
3 – needle valve
4 – flow meter
5 – flow controller
6 – steam generator
7 – condensate drain
8 – scissor hoist
9 – oven
10 – preheat zone

11 – sample zone
12 – superheater
13 – thermometer
14 – reactor bypass
15 – cooler
16 – flow meter
17 – IR spectrometer
18 – gas meter
19 – bypass
20 – gas outlet

Experimental apparatus

Gas flow controller

Oven
(in working position)

Scissor hoist

Boiler regulator

Superheater
regulator

IR spectrometer

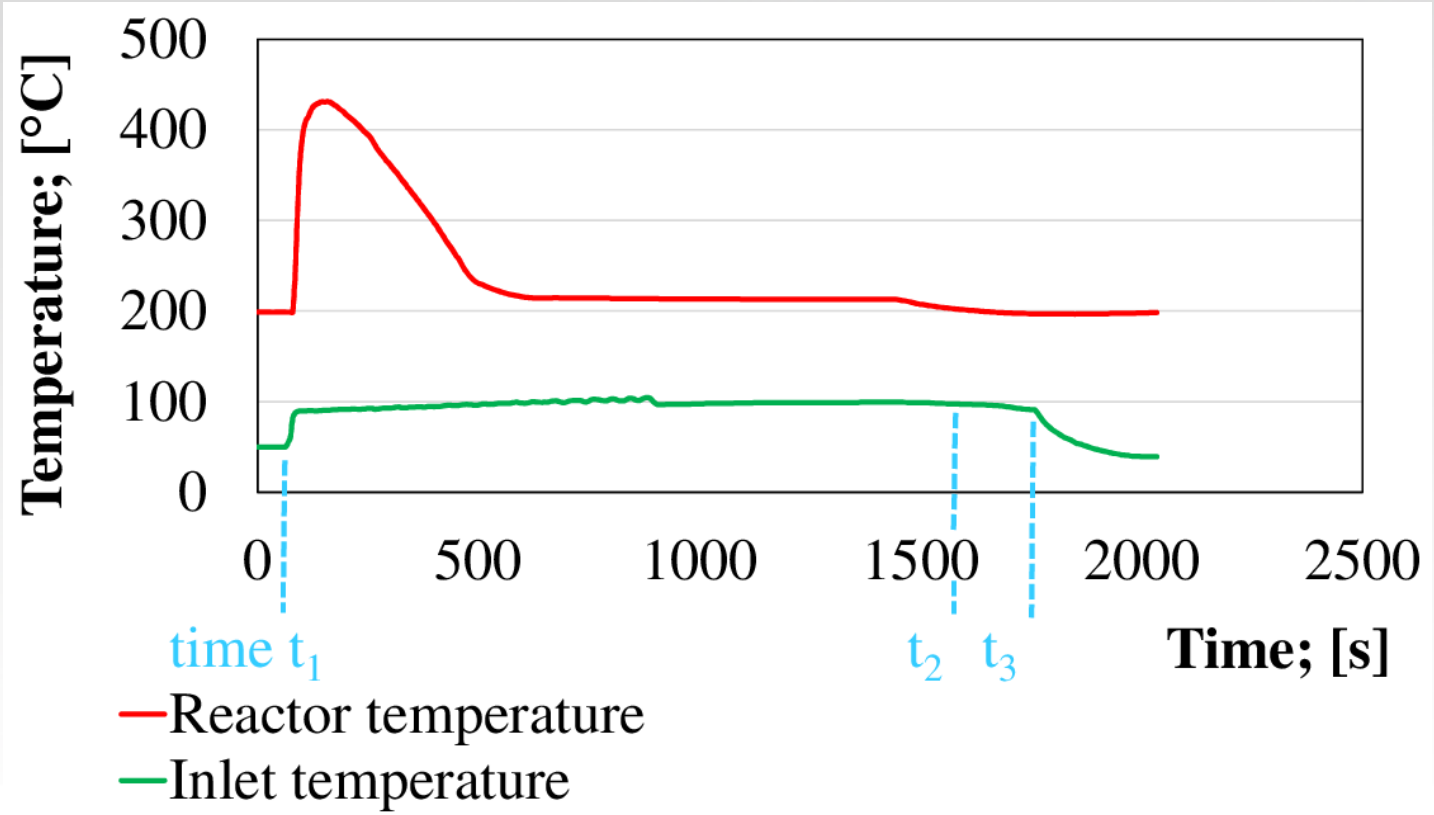
Condensate drain

Principle of steam reactivation

Capacities compared between treated samples and the samples without this step

Course of periodical reactivation:

- after calcination at 850 °C the sample cooled down and water vapour introduced into its layer at 100 – 350 °C.
- generated $Ca(OH)_2$ subsequently decomposed at 650 °C.



Basic results

overview of capacity changes

Cyclical calcinations/carbonations without reactivation step:

in 1st cycle 6.1 – 37.1 g.100 g^{-1}

in 6th cycle 1.2 – 15.6 g.100 g^{-1}

If model gas contains residual SO_2 (0.3 mol. %) – dramatical capacity drop:

in 6th cycle e.g. best sample 15.6 ⇒ 5.3 g.100 g^{-1}

Cyclical calcinations/carbonations with periodical reactivation :

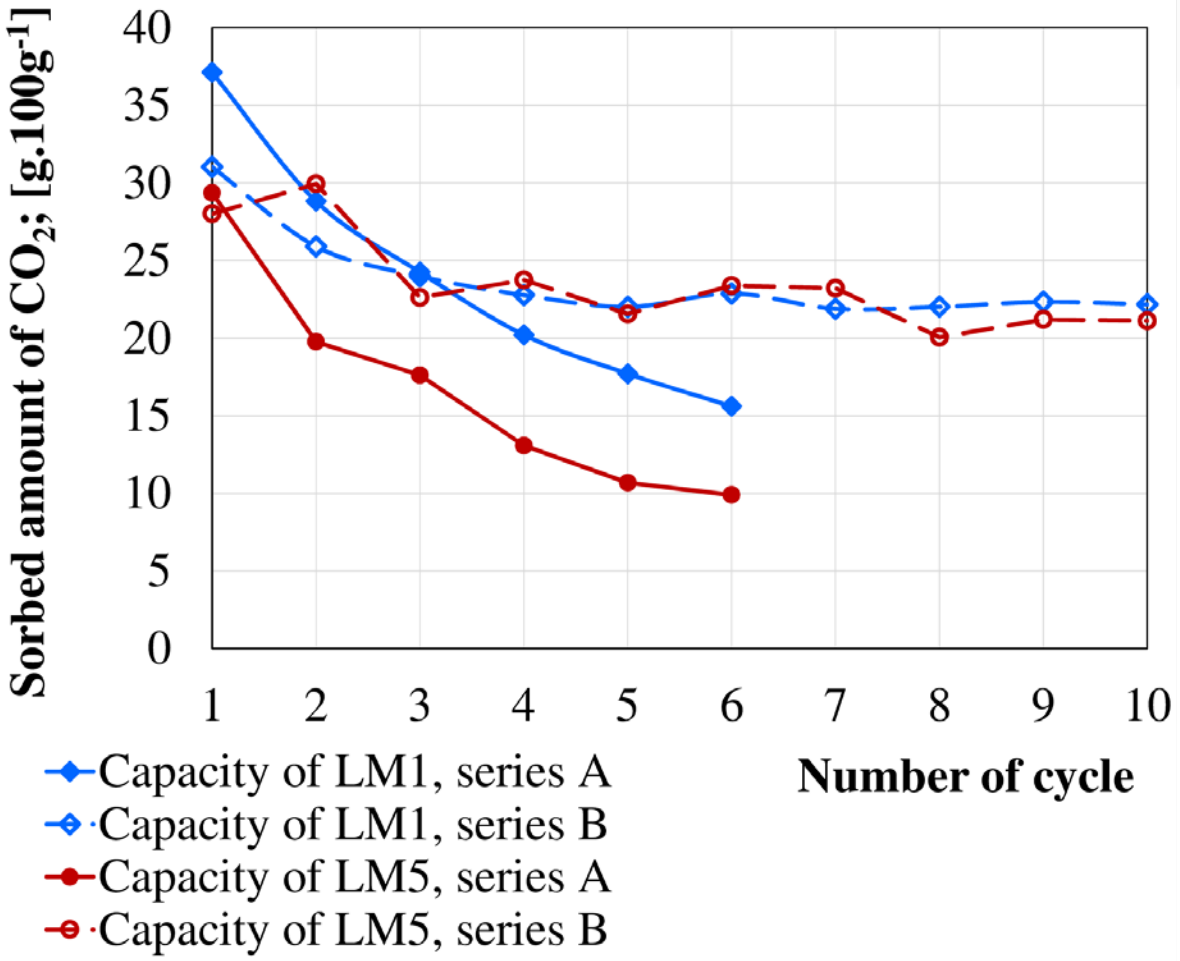
in 10th cycle >22 g.100 g^{-1} (for the best and average sample)

Highest $CaCO_3$ content = highest capacity after steam reactivation ? ..... **NO !** **Key question = why?**

Comparison of capacities with and without steam reactivation

LM1:
Quarry ”Čertovy schody”

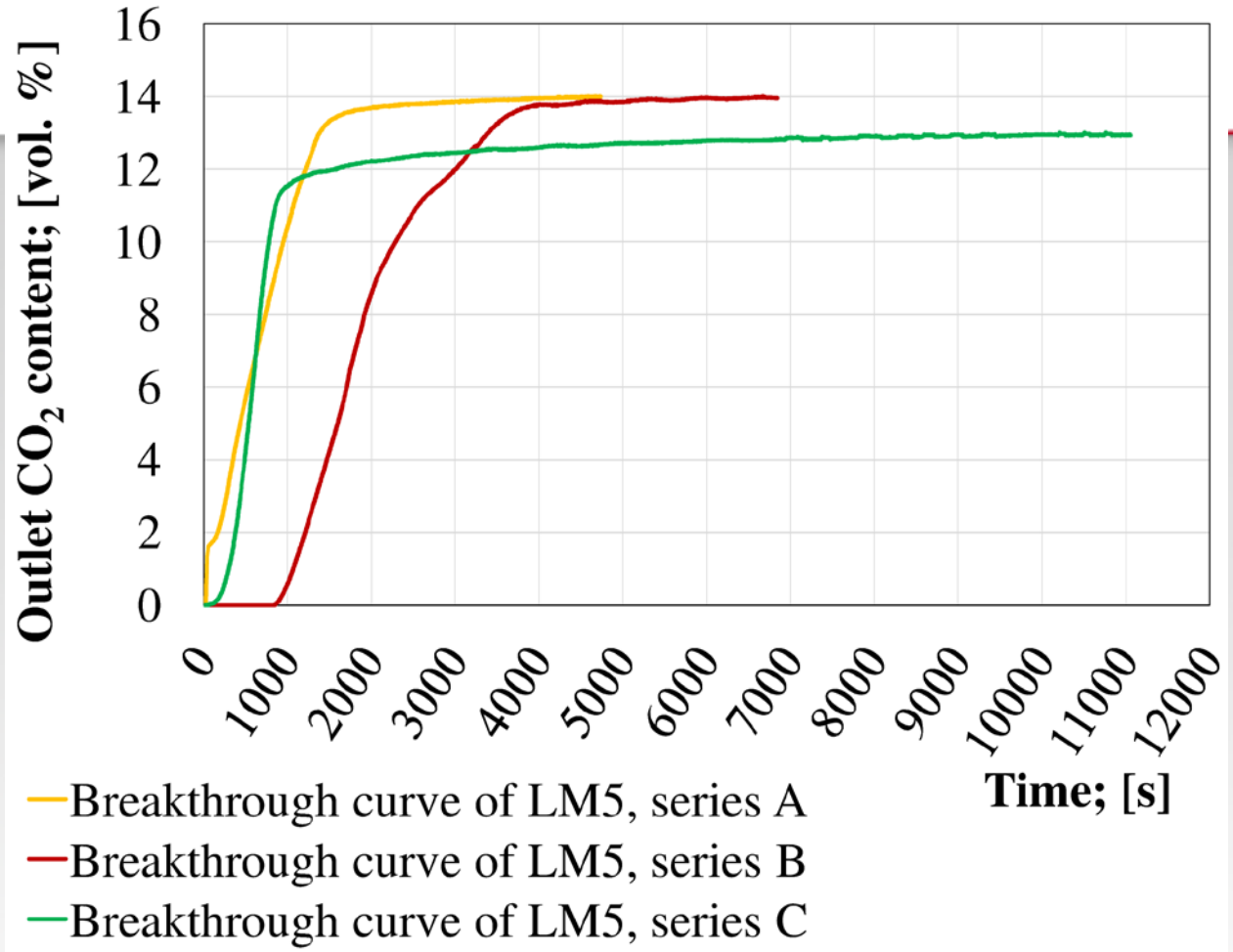
LM5:
Quarry ”Libotín”



Legend:

LM1 → best sample during tests without regeneration (series A)
LM5 → average sample in series A
Tests with periodical reactivation = series B)

Comparison of shapes of breakthrough curves in 5th cycle



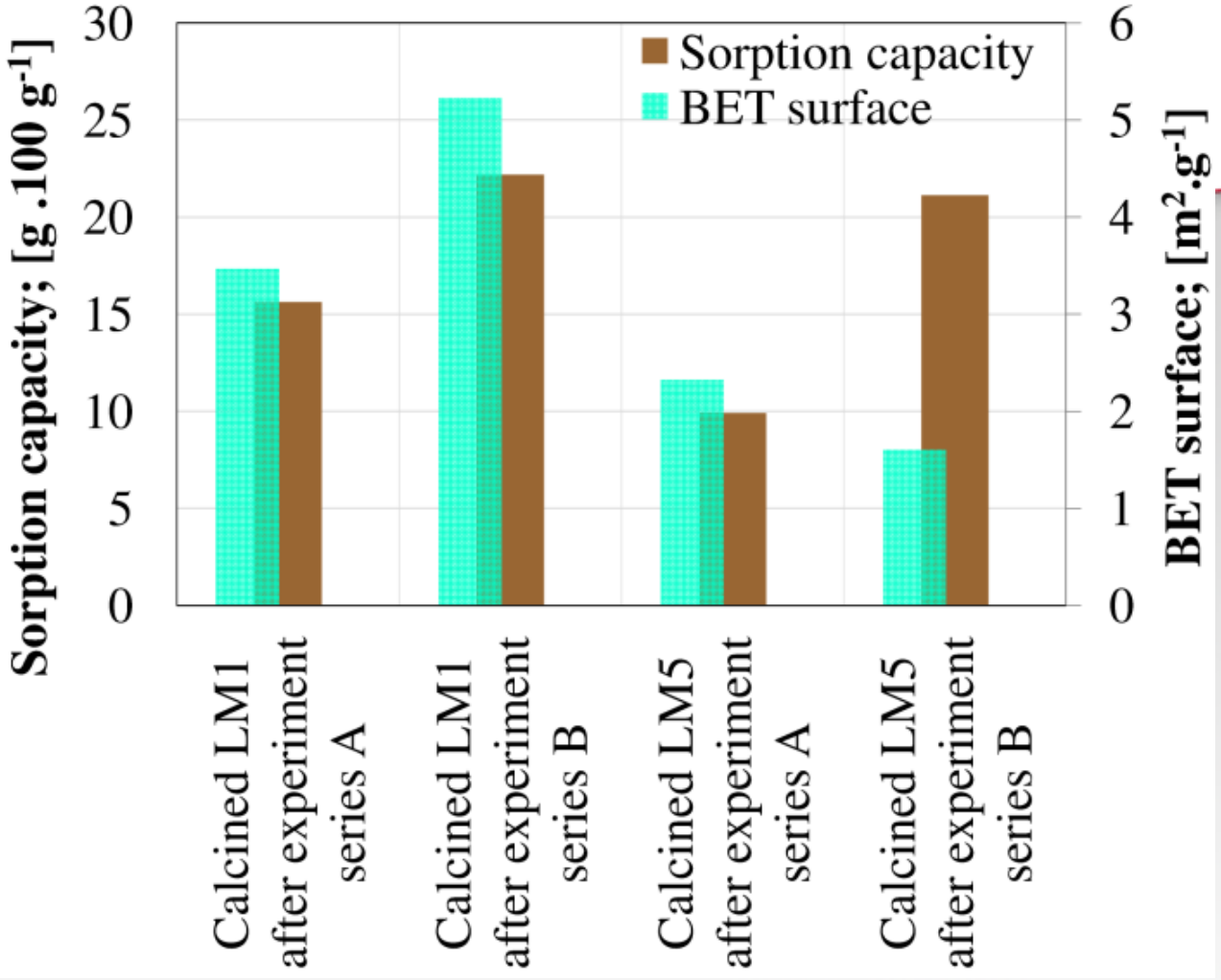
Legend:

Series A → tests without regeneration

Series B → tests with periodical steam reactivation

Series C → tests with 0.3 mol. % of SO_2 in the gas mixture

Comparison of specific surface



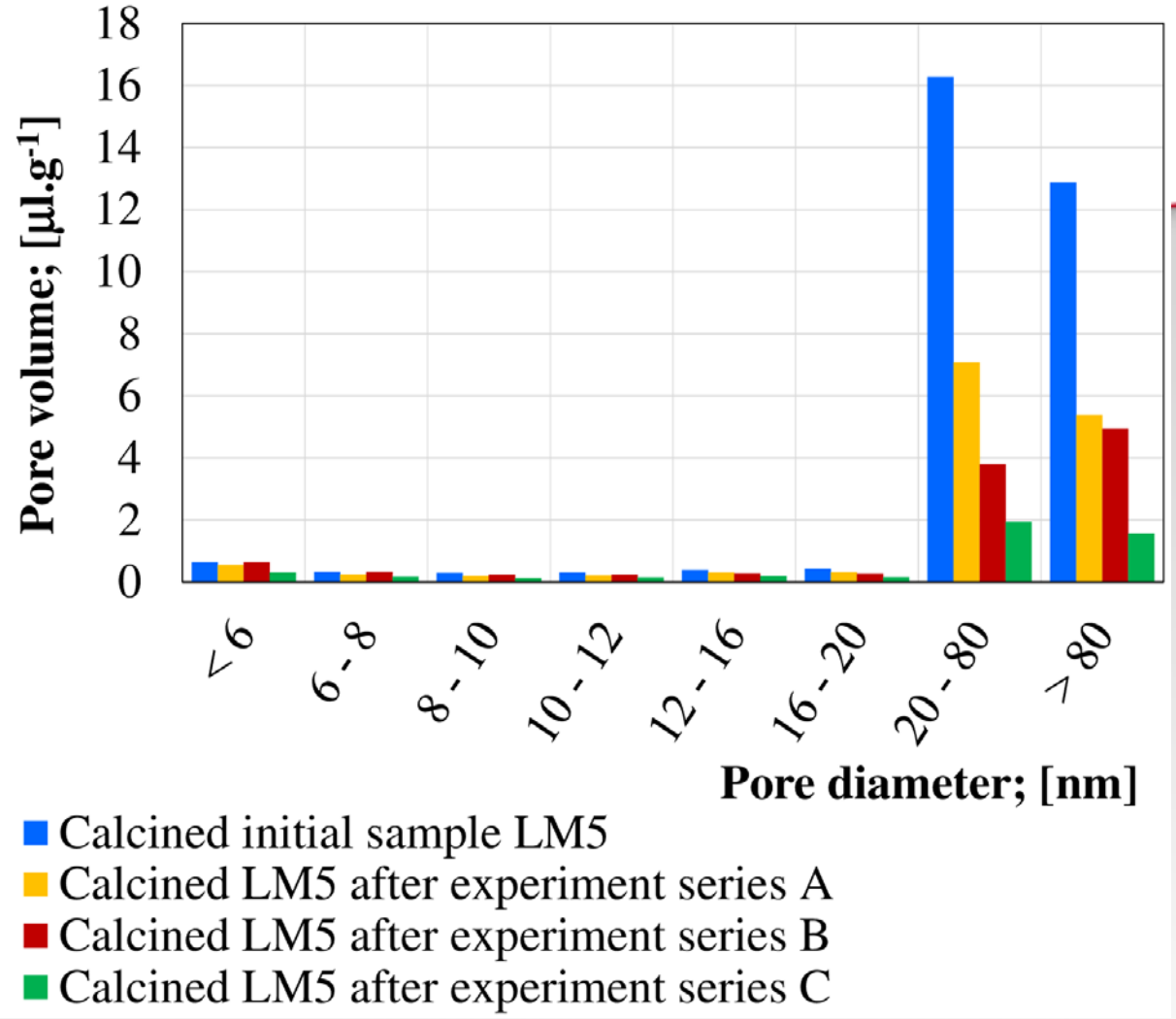
Legend:

LM1 → best sample during tests without regeneration (series A)

LM5 → average sample in series A

Tests with periodical reactivation = series B)

Comparison of pore sizes distribution



Legend:

Series A → tests without regeneration

Series B → tests with periodical steam reactivation

Series C → tests with 0.3 mol. % of SO_2 in the gas mixture

Summary of experiments with limestones

Limestones as natural raw material = low purchase costs but high potential for CCS

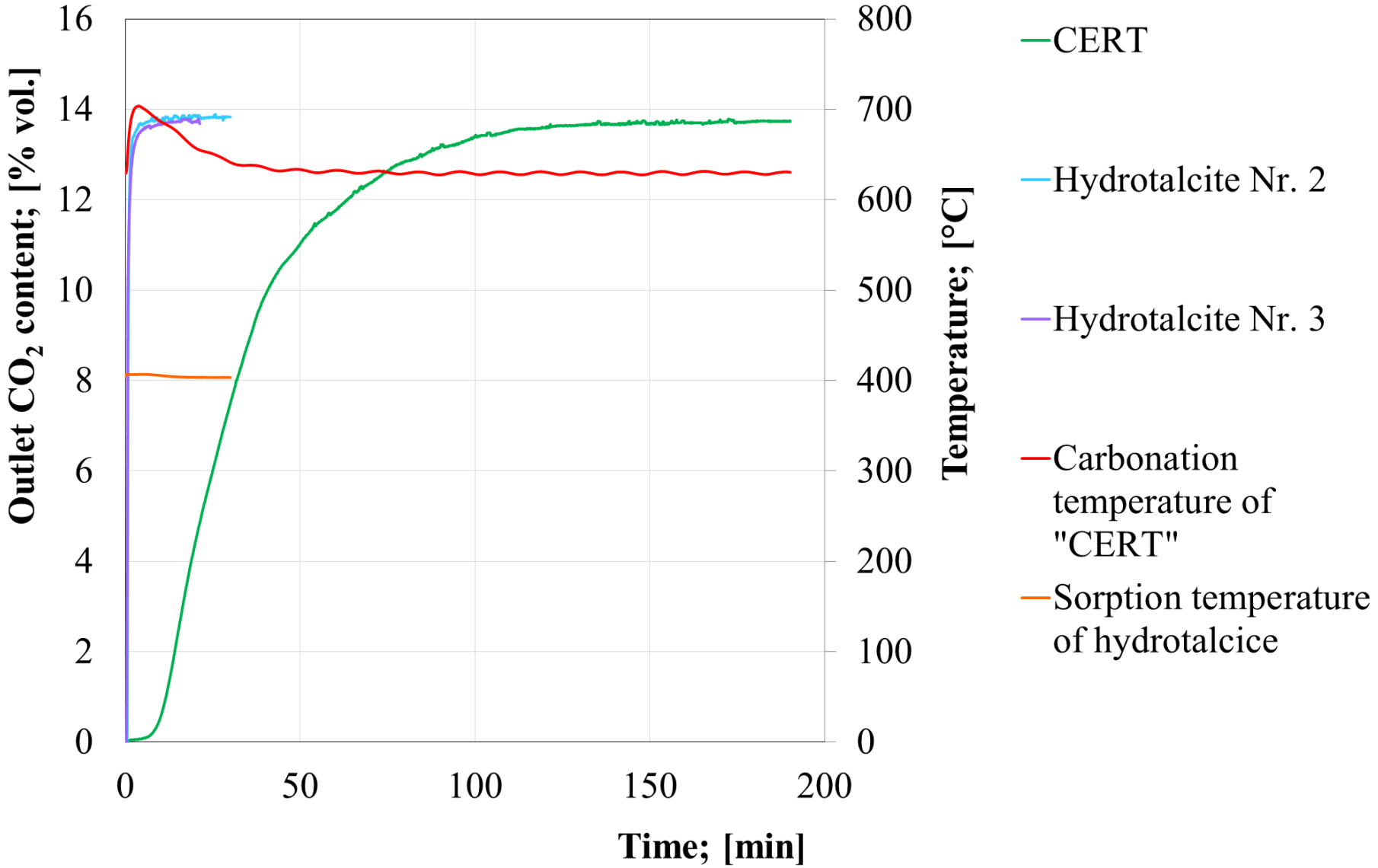
- Confirmed suppression of the sorption capacity decrease using steam hydration,
- no significant differences between hydration by saturated vapor or superheated steam,
- high average equilibrium capacity over 22 g.100 g^{-1} and sustainable technical transfer capacity 20.4 g.100 g^{-1} in case of reactivation,
- no relation among BET surface, pore size distribution and capacity when steam reactivation is applied, steam destructs sintered pores with diameter >>> 80 nm.
- even low SO_2 concentration significantly decreases capacity, but $CaSO_4$ cracks sintered surface $\rightarrow$ increased sorption rate in the initial phase of the process.

What's better: limestones or HTLcs ?

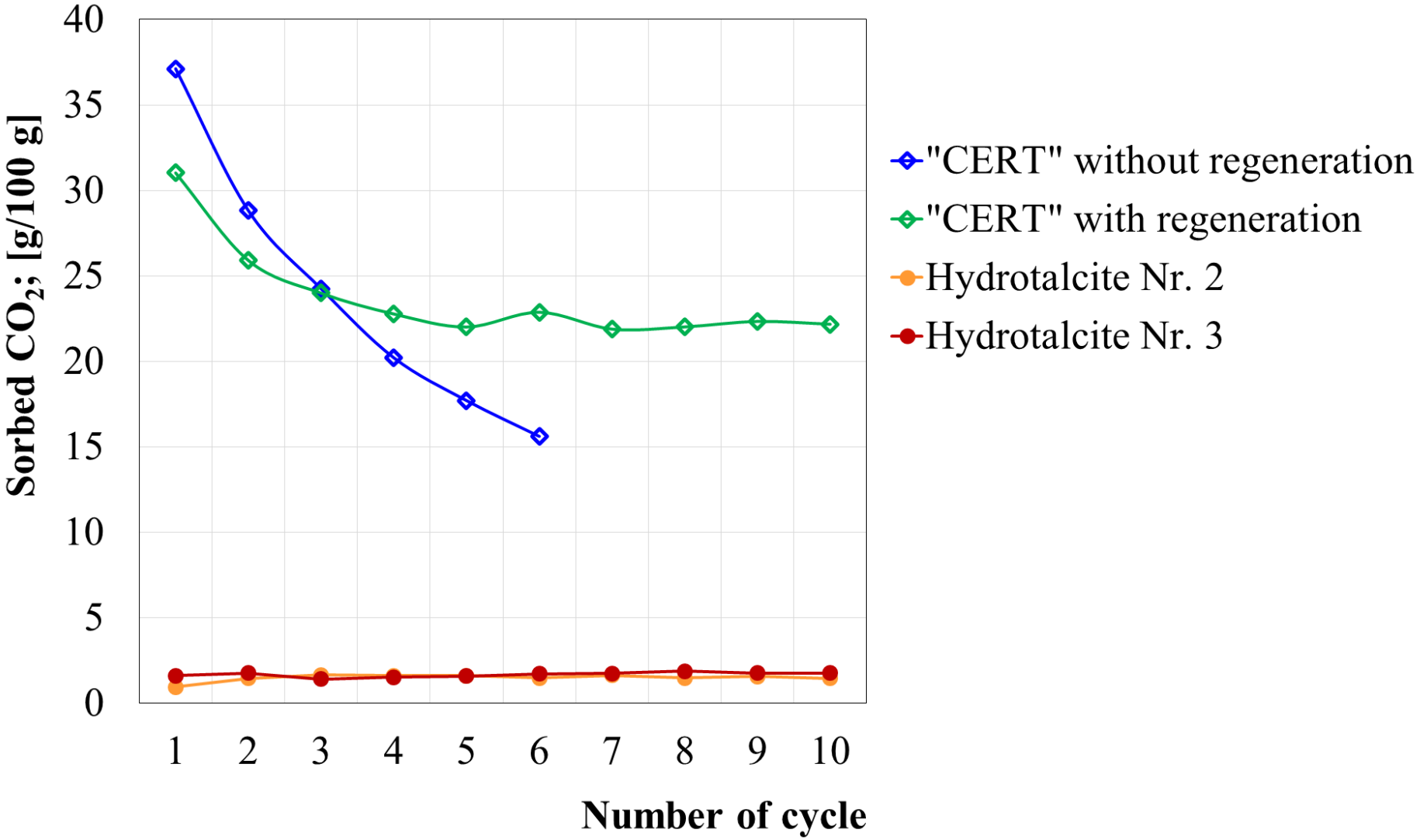
Hydrotalcite-like compounds published as highly promissing sorbents

- Compared parameters:
  - Equilibrium sorption capacities,
  - Technically usable transfer capacities,
  - Changes in sorption capacities due to number of sorption / desorption cycles.

Comparison of shapes of breakthrough curves in 10th cycle



Comparison of equilibrium sorption capacities



Summary and conclusions

- **Properties of HTLcs**
  - In fact no changes in sorption capacities during cycles,
  - very fast sorption / desorption,
  - almost identical equilibrium and technical transfer capacity,
  - low average capacity 1.5 g/100 g for non-impregnated and 1.8 g/100 g for impregnated sorbent,
  - lower working temperatures 400 °C and 500 °C, respectively.

- **Properties of limestones**
  - Possibility of suppression of the sorption capacity decrease using hydration by water vapour,
  - high average equilibrium capacity 22.3 g/100 g in case of vapour regeneration,
  - technical transfer capacity 20.4 g/100 g is lower, however, better by order of magnitude if compared with hydrotalcite,
  - natural raw material = lower purchase costs.

Thank you!